ASSESMENT OF HEAVY METAL IN SOIL FROM ACTIVE SAWMILL VICINITY

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ABSTRACT
In this study, soil profiles of four active sawmill vicinity were investigated for physiochemical properties and heavy metals concentration. Particle size distribution of soil showed a preponderance of sand fraction, followed by clayed and silt, classifying the soil to be sandy loam. The pH values of study soil were slightly acidic to slightly basic region (5.8±0.02 to 8.1±0.04). This pH region is an indication that the soil will drained. Soil sample from control site (Mn = 5.20± 0.02, Cu = 8.10± 0.04, Cr = 2.51± 0.00) revealed low metal concentration than the soil collected from the sawmill vicinity. These results suggest that heavy metal concentration is from anthropogenic sources (sawdust and other wood waste materials). The risk assessment of the study soil determined in terms of mobility factor, contamination factor and ecological risk factor indicate that the soil is polluted with respect to these heavy metals, Mn,Cu and Cr. It was advocated that the federal and state ministry of environment should routinely monitor sawmill vicinity soil in order to ensure a reduction in the level of contamination by heavy metal.
Keywords: Soil, heavy metal, risk assessment, sawmill

INTRODUCTION
Production activities is one of the major environmental threat as it releases broad spectrum of harzadous wastes (Wuana and Okieimen, 2013), such as heavy metal into the soil environment. Heavy metals top the list of inorganic pollutant due to their toxicity and persistence in the soil. There are radical soil chemistry changes that can arise from the presence of co- contaminant chemicals even at low concentration. The fate and mobility of metal in soil environment rely significantly on chemical form and metal speciation. In the soil, heavy metals are adsorbed by initial fast reaction minutes (hours) followed by slow adsorption reaction (days, years) and are redistributed into different chemical forms with varying bioavailibitity, mobility and toxicity (Schiowatana*et al.,* 2001). The major concern of soil pollution is that there are many production or industrial sites where people are in direct contact to soil. Other mechanisms include contamination of drinking water or inhalation of soil contaminants which have vapourised. Effects of heavy metal toxicity on human ranges from mild eyes, nose and skin irritations through severe headache, diarrhea, hemates, vomiting, dizziness to organ failure, miscarriages and cancer etc. Recent studies has shown that carbonized sawdust obtained from wood sawmill sites contained heavy metals (micro nutrients) (Ugbune and Okou, 2019). These waste litter the sawmill soil vicinity and bioaccumulate with time. The organic portion of the waste is degraded by microorganisms leaving inorganic (heavy metals) portion thereby contaminating the soil. Heavy metals in these waste can also leached down or washed into river to cause ground water and surface wate pollution respectively. The heavy metal can passed to man through food chain or direct contact. High concentration of manganese in soil causes swelling of cell walls, weathering of leafs and brown spots in leaves.High dose of copper can cause anaemia and intestine irritation. Long term exposure of chromium through food , air and water can cause kidney and liver damage. It become necessary to evaluate the levels of physiochemical properties, heavy metal concentration, spatial distribution and ecological health of soils from sawmill vicinity.

Collection and Preparation of Soil Sample
Soil samples were collected from four active sawmill vicinity in sapele town (5° 53' 38″ N, 5° 40'35" E), Nigeria, namely Ogoro Water Side I, Sapele Town (1); Ogoro Water Side II, Sapele Town(2); Uguadja I, Sapele Town (3); Uguadja II , Sapele Town(4). At each sample sites , soil sample were collected within 10 cores of W-shape. The soil collected from each core at a given site was combined to form a representative sample. In the laboratory, the soils were dried at ambient temperature (28°C), crushed in a porcelain mortar and sieved through a 2mm stainless sieve. Samples were stored in polythene bag and properly labelled prior analysis.

Methods

Soil pH was determined by Black method, Ugbune and Okuo 2011. The hydrometer method described by Bouyoucos,Ugbune and Okuo,2011 were used in evaluating particle size distribution. All reagents used for the preparation of standard solution and analysis were analytical grades (BDH or Sigma).

Fractionation of metal in soil was assessed using sequential extraction procedures according to Tessiers Scheme(Tessier*et al.,* 1979., Ugbune and Okuo, 2011).

Extraction of exchangeable metals**,** 8mL of 1M magnesium chloride (pH 7.0) was added to 1g of soil sample in a 50mL polypropylene bottle and the mixture was shaken in a mechanical shaker for 1hr.

Extraction of carbonates bound metals,8mL of 1M sodium acetate solution was added to the residue and adjusted to pH 5.0 with concentration acetic acid. The mixture was agitated for 5 hrs in a mechanical shaker.

Extraction of Fe-Mn oxides bound metals, 20 mL of 0.04 M hydroxylamine hydrochloride in 25% acetic acid was added to the residue and the mixture heated was 96 ± 3^0C with occasional agitation for 6 hrs.

Extraction of organically bound metals, 3mL of 0.02M nitric acid and 5mL of 30% hydrogen peroxide were added to the residue and adjusted to pH 2 with nitric acid. The mixture was heated to 85 ± 2^0C in a water-bath for 2 hrs with occasional agitation. An additional 3mL aliquot of the acidified 30% hydrogen peroxide was added and the mixture was heated at $85 \pm$ 2^0C for 3 hrs with intermittent agitation. 5mL of 3.2M ammonium acetate in 20% nitric acid was added to the cooled mixture and the sample was diluted to 20mL and stirred continuously for 30mins.

Extraction of residual forms of metals,the residue from the previous extraction was transferred into a digested tube and digested with 5mL of nitric acid and 1mL of perchloric acid until white fumes appeared. The tube was cooled and the side rinsed with distilled water and filter through a Whatman 1 filter paper into a 100mL volumetric flask. The volume was made to mark with water.

The concentration of heavy metals (Mn, Cu and Cr) in the various extract were determined in a pre-caliberated Atomic Absorption Spectrophotometer.The concentrations of the metal solutions used for the caliberation were 2-20ppm.

RESULT AND DISCUSSION

The pH of result of soil (Table 1) obtained from active sawmill sites is slightly acidic to basic region (5.8±0.02to 8.1±0.04). Slightly low pH is an indication that the metal will be in soil solution and therefore bioavailable as metal do not form complex at low pH. Result of particle distribution of soil (Table 1) showed 21.75.±0.03 to 25.36±0.05% clay, 2.15±0.01 to 2.19±0.00% silt and 72.48±0.05 to 76.10±0.04% sand, classifying the soil to be sandy loam. These results indicate that the soil is relatively porous, permeable and well drained.

Table 1: Physiochemical Properties of Soil

Sites	pH	Sand (%)	Clay (%)	Silt (%)
1	5.8± 0.02	75.25± 0.07	22.56± 0.05±	2.19± 0.00
2	7.9± 0.03	72.48± 0.05	25.36 ±0.05	2.16± 0.01
3	7.8± 0.03	74.53± 0.09	23.31± 0.06	2.17 ± 0.00
4	8.2± 0.04	76.10± 0.04	21.75± 0.03	2.15 ±0.01

Soil from the four sawmill sites indicate higher concentration of the heavy metals manganese(Mn), copper (Cu), chromium (Cr) when compared to metal concentration obtained from 30 meter away from wood sawmill vicinitys serving as control (Table 2).

Table 2 Heavy Metal Concentration in Sawmill Vicinity

	Heavy	Metal	Concentration
Sites	Mn(ppm)	Cu(ppm)	Cr(ppm)
1	18.20± 0.22	20.9±0.05	15.16± 0.09
2	11.62± 0.21	24.15± 0.09	10.12± 0.04
3	12.15± 0.22	22.38± 0.02	13.52± 0.05
4	19.60±0.25	22.04± 0.03	14.620.06
control	5.20± 0.02	8.10± 0.04	2.51± 0.00

Manganese is a micro-nutrient that plant needs in small quantity but become toxic to soil at higher concentration. Result of manganes in the sample soil ranged from 11.62 ∓ 0.21 to 19.60 ∓ 0.05 ppm higher than the background concentration. Manganese in site 4 have the highest concentration, this might be attributed to the age of of production activities. Copper in sites 2 (Table 2) have the highest concentration while that of site 1 have the lowest concentration. Copper concentration in the sample soil is higher than the control, suggesting that copper contamination is from anthropogenic sources. Copper concentration of study soil is within the range reported by Okieimen and Ilori, 2013. Chromium assessment in sample soil falls within 10.12 ∓ 0.04 to 15.16 ∓ 0.09 ppm, these values are higher than the concentration of control, however it is within the range reported by Adeyeye *et al.,* 2018. In general,heavy metals concentrations in all the sample sites are higher than the control sample, suggesting that metals concentrations are from anthropogenic sources.

Metal Fractionation

Sequentia extraction methods were adopted in this study to assess the distribution pattern of Mn, Cu, and Cr among the operational define pool in contaminated soil (Okieimen and Ilori, 2011).The fractionation result revealed that the concentration of Mn was mainly in the residual fraction(5.22 ∓ 0.00 to18.62 ∓ 0.09). Higher concentration of Mn in these fraction is an indication that Mn will be relatively stable. The residual fraction, had a higher concentration with a range of 4.06 ∓ 0.01 to $29.96 \mp .0.06$. Exchangeable and carbonate pool of Cu in site 1 is higher when compared to other fraction (Table 3) . This suggest that metal in the site will be relatively mobile. Heavy metals in exchangeable and carbonate fraction have been said to be more mobile and bioavailable (Bacon and Davidson, 2009).

Exchangeable and carbonate fraction of Cr in soil had the lowest level of fraction. Residual had the highest. Residual fraction is considered the most stable, less reactive and less bioavalable since it is occluded within the crystal lattice layer of silicate and well crystallized oxide minerals (Seggrara *et al.,* 2008., Abel *et al.,* 2007 Schawarzonbach *et al.,* 1993).

Table 3: Fractionation of Heavy Metals in Sawmill Vicinity Soil

Sites	Fraction	Mn	Cu	Cr
	Exchangeable	2.31±0.00	2.41±0.20	1.06±0.01
1	Carbonate	3.2±0.21	3.5±0.02	1.98± ± 0.00
	Fe-Mnoxide	4.00±0.00	4.21± 0.05	3.145± 0.01
	Organic	4.200 ± 00.00	4.61±0.02	4.81± 0.25
	Residual	4.90 ± 0.06	6.25±0.05	5.00±0.01
	Exchangeable	1.05±0.01	1.06±0.01	1.06 ±0.01
	Carbon	2.11± 0.02	2.11±0.00	1.09 ±0.00
2	Fe-mn oxide	2.5 ±0.05	4.32±0.02	2.14 ±0.04
	Organic	2.98±0.05	7.62±0.03	2.82± 0.02
	Residual	3.26±0.01	9.52±0.02	3.21 ±0.02
3	Exchangeable	1.08±0.00	1.09±0.02	1.02±0.00
	Carbon	2.11±0.01	2.05±0.03	1.01±0.01
	Fe-mn oxide	2.68±0.02	6.00±0.01	3.02±0.02
	Organic	2.99±0.03	6.06±0.02	3.65±0.02
	Residual	4.05±0.02	8.05±0.01	4.05±0.03
	Exchangeable	2.06±0.01	2.01±0.00	1.06±0.00
	Carbon	3.82±0.02	2.00±0.02	1.02±0.00
4	Fe-mn oxide	4.00±0.02	3.25±0.02	2.06±0.02
	Organic	4.05±0.01	3.87±0.03	3.77±0.02
	Residual	5.22±0.00	4.06±0.02	3.92± 0.01

Mobility Factor: Metal mobility relative indices is calculated as mobility factor (MF) (Kabala and Singh,2001) as shown in equation 1

$$MF = \frac{exch.+carb.}{exch.+ carb.+FE-mn +orga.+ res.} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ (1)}$$

Mobility factor explained the potential mobility of metal. High mobility is a symptom of relative high liability and bioavailability of metal in soils. Results obtained inTable 4 indicate that mobility factor of heavy metal in soil samples range from 0.13 ∓ 0.01 to 0.31 ∓ 0.02 for all the locations. High mobility suggest that metal is from anthropogenic sources. This interpret the relative high liability and bioavailabity of heavy in soil (Ugbune and Okuo, 2011., Kabala and

Singh, 2001). Metal mobility results for for all metal in studies soil follow the order: Mn> Cu >Cr. The MF values in different sites indicate that metal will be available for plant uptake in all the soil profiles. MF result falls within the range reported by Ugbune and Okuo,2011, Okuo*et al,* 2019 in battery work site soil and road side soils respectively.

Table 4: Mobility of Heavy Metals in Soil

Sites	Mn	Cu	Cr
1	0.30±0.01	0.20±0.00	0.19±.0.00
2	0.27±0.02	0.13±0.01	0.21±0.01
3	0.25±0.00	0.14±0.01	0.16±0.02
4	0.31±0.01	0.26±0.00	0.18±0.00

Environmental risk factor (ERF) was used to asses environmental risk in order to establish potential threat of heavy metal (Saenz *et al.,* 2003). ERF was obtained using equation 2

$$ERF = CSQV - \frac{ci}{csqv} \text{..........................(2)}$$

When ERF < 0, there is potential ecological threat., ERF >0, no potential ecological threat to living things. Result obtained from Table 5 suggest that Mn, Cu and Cr in the sites will pose environmental threat to living organisms as ERF were less than zero.

Table 5:Environmental Risk Factor of Heavy Metal in Soil

Sites	Mn	Cu	Cr
1	-1.80 ±0.01	-2.80±0.02	-1.20±0.01
2	-1.63±0.00	-0.17±0.01	-1.21 ±0.00
3	-0.21±0.00	-.089±0.02	-1.15±0.01
4	-1.67±0.01	-1.74±0.01	-1.01 ±0.00

Contamination factor (CF) was used to evaluate the level of contamination of the study soil by the heavy metals (Lin *et al.,*2009). The contamination factor was calculated using equation 3

$$CF = \frac{ci}{csq} \text{.. (3)}$$

Where CSQ = concentration of soil/ sediments values (heavy metal concentration in residual fraction of soil which is equivalent to the background concentration/ pre-industrial concentration)

Ci = heavy metal concentration in the first fraction of soil. When the concentration factor CF< 1 refers to low concentration.,1 $\leq$CF<3 means moderate concentration., 3$\leq$CF$\leq$6 indicates considerable contamination and CF>6 indicate very high contamination. Contamination factor indicate that Cu in sites 1 showed considerable contamination while other metal in the sites showed moderate contamination except Cr in site 4 with respect to all the heavy metals.

Table 6: Contamination Factor of Heavy Metal in Soil

Sites	Mn	Cu	Cr
1	2.80± 0.02	3.79±0.02	2.20 ±0.01
2	2.67±0.02	1.59±0.00	2.21±0.02
3	2.11±0.01	1.89±0.00	2.15±0.02
4	2.06±0.01	2.01±0.02	0.27±0.00

CONCLUSION

Studies of soil within sawmill indicates high level of metal concentration when compared to background concentration. Chemical fraction of heavy metal in the first two fraction were

considerable high and can be found in the soil solution and therefore bioavailable for plant adsorption. Mobility factor suggest that heavy metal in the soil is relatively mobile and can enter food chain.

Contamination factor and ecological factor in this studies soil revealed that heavy metal will posed potential health risk to living organisms. It is therefore, recommended that proper handling of waste and remediation should be adopted in sawmill vicinity soil

REFERENCES

Adeyeye,E.I., Shiltu,O.S., Ayodele, O.J. Ilori O.A. (2018). Heavy metal pollution potential in soil influenced by sawmill operations at Ado-Ekiti; Nigeria.*Bangladesh .J.Sci.Ind Res.,*53(1): 29-34.

Bacon, J.R., Davidson, C.M. (2008). Is there future for sequential chemical extraction? 133:25-46. *Journal of Environmental Quality,* 30(6) :1940-1949.

Kabala,C and Singh, B.R. (2001). Fractional and mobility of copper, lead and zinc in soil profile in the vicinity of a copper Smelter .*J. Enviorn. Qual.,30:485-495.*

Lin,J., Cai,M., Qi, A and Hu,H. (2009). Contamination level and speciation of heavy Metals in sediments from Youdaglake,Xiam. 1 ECS Second international conference on environmental and computer Science, 28-30 December, 48-53.

Okieimen,F.E and Illori,G.E. (2013). Chelant extraction of heavy metals for the remediction of CCA contaminated soils. *Geo Environmental & Climate Change Adaptation Research,*3:1-33.

Okuo,J.M., Anegbe,B., Emina,R.A., Chiedu I.E. and Ugbune,U. (2019).Speciation of heavy Metals in roadside Soil in major traffic intersections along Ugbowo Lagos Road of Benin City, Edo State Nigeria.*Journal of Applied Science,* 3:50-64.

Saenz, M, Blasco,J and gomezpara,A (2003). Speciation of heavy Metals Ecosystems in the Gulf of Cadiz, Southwest.*Iberian PerisulaEnviornmental Toxicology,*22 (12): 33-39.

Schiowatana,J, Mclaren, R.G, Chanmecha,N, and Samphe, A (2001). Fractionation of soil by a contineous-flow sequential extraction methods" 45.

Tessier, A, Campbell, P.G.C, and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem*. 51: 844-851.

Ugbune, U and Okuo, J.M.(2019).Effect of carbonized sawdust briquette on the nutrient status of dumpsites Soil.*Nigerian Journal of Applied Science,* 37:1-10.

Ugbune,U and Okuo, J.M. (2011). Sequential fractionation and distribution of heavy metals in soil from battery work sites. *Nigeria Journal of Applied Science,* 2:132-141*.*

Wuana,R.A and Okieimen, F.E. (2013). Evaluation of heavy metal speciation in single and multi-metal contaminated soil by BCR sequential extraction,*Nigerian Journal of Applied Science,* 2:87-102*.*